

6-29-00

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Practitioner's Docket No. 50439-2 CIP

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
 Assistant Commissioner for Patents
 Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): **Leon R. Barstad, James E. Rychwalski, Mark Lefebvre, Stephane Menard,
 James L. Martin, Robert A. Schetty, III and Michael Toben**

WARNING: 37 CFR 1.41(a)(1) points out:

"(a) A patent is applied for in the name or names of the actual inventor or inventors.

(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(i) is filed supplying or changing the name or names of the inventor or inventors."

For (title): ELECTROLYTIC COPPER PLATING SOLUTIONS

CERTIFICATION UNDER 37 C.F.R. 1.10*

(Express Mail label number is *mandatory*.)

(Express Mail certification is *optional*.)

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on this date June 28, 2000, in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EK493794156US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

Deanna M. Rivernider

(type or print name of person mailing paper)

Deanna M. Rivernider
 Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

***WARNING:** Each paper or fee filed by "Express Mail" *must* have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).
 "Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will *not* be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

1. Type of Application

This new application is for a(n)

(check one applicable item below)

- ☐ Original (nonprovisional)
- ☐ Design
- ☐ Plant

WARNING: Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.

WARNING: Do not use this transmittal for the filing of a provisional application.

NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

- ☐ Divisional.
- ☐ Continuation.
- ☒ Continuation-in-part (C-I-P).

2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

NOTE: A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. 112. Each prior application must also be:

- (i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or
- (ii) Complete as set forth in § 1.51(b); or
- (iii) Entitled to a filing date as set forth in § 1.53(b) or § 1.53(d) and include the basic filing fee set forth in § 1.16; or
- (iv) Entitled to a filing date as set forth in § 1.53(b) and have paid therein the processing and retention fee set forth in § 1.21(l) within the time period set forth in § 1.53(f).

37 CFR 1.78(a)(1).

NOTE If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

WARNING: *When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application **must** be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).*

☒ The new application being transmitted claims the benefit of prior U.S. application(s).
Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE
BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

3. Papers Enclosed

A. Required for Filing Date under 37 C.F.R. 1.53(b) (Regular) or 37 C.F.R. 1.153 (Design) Application

18 Pages of Specification (including cover sheet)

3 Pages of Claims

2 Sheets of Drawing

☐ Formal

☐ Informal

B. Other Papers Enclosed

1 Pages of Abstract

 Other

WARNING: ***DO NOT** submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 C.F.R. 1.84, see Notice of March 9, 1988 . . . (1990 O.G. 57-62).*

NOTE: *"Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page." 37 C.F.R. 1.84(c)).*

(complete the following, if applicable)

☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. 1.84(b).

4. Additional Papers Enclosed

- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement (37 C.F.R. 1.98)
- ☐ Form PTO-1449
- ☐ Citations
- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other:

5. Declaration or Oath

NOTE: *A newly executed declaration is not required in a continuation or divisional application provided the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47 then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 CFR 1.63(d).*

NOTE: *A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name, including the family name, and at least one given name without abbreviation together with any other given name or initial, and the residence, post office address and country of citizenship of each inventor and state whether the inventor is a sole or joint inventor. 37 CFR 1.63(a)(1)-(4).*

- ☐ Enclosed

Executed by

(check all applicable boxes)

- ☐ inventor(s).
- ☐ legal representative of inventor(s). 37 CFR 1.42 or 1.43.
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
- ☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. See item 13 below for fee.

- ☒ Not Enclosed.

NOTE: *Where the filing is a completion in the U.S. of an International Application, or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

- ☐ Application is made by a person authorized under 37 C.F.R. 1.41(c) on behalf of all the above named inventor(s).

(The declaration or oath, along with the surcharge required by 37 CFR 1.16(e), can be filed subsequently).

NOTE: It is important that all the correct inventor(s) are named for filing under 37 CFR 1.41(c) and 1.53(b).

☐ Showing that the filing is authorized.
(not required unless called into question. 37 CFR 1.41(d))

6. Inventorship Statement

WARNING: If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.

The inventorship for all the claims in this application are:

☐ The same.
or
☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,
☐ is submitted.
☐ will be submitted.

7. Language

NOTE: An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of \$130.00 required by 37 CFR 1.17(k) is required to be filed with the application, or within such time as may be set by the Office. 37 CFR 1.52(d).

☒ English
☐ Non-English
☐ The attached translation includes a statement that the translation is accurate. 37 C.F.R. 1.52(d).

8. Assignment

☒ An assignment of the invention to Shipley Company, L.L.C. of
Marlborough, Massachusetts 01752
☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.
☐ was filed in the parent application
☐ will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment" Notice of May 4, 1990 (1114 O.G. 77-78).

WARNING: A newly executed "STATEMENT UNDER 37 CFR 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.

9. **Certified Copy**

Certified copy(ies) of application(s)

Country	Appln. No.	Filed
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from which priority is claimed

- ☐ is enclosed.
☐ was filed.
☐ will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. **Fee Calculation (37 C.F.R. 1.16)**

A. ☒ Regular application

CLAIMS AS FILED					
Claims	Number Filed	Basic Fee Allowance	Number Extra	Rate	Basic Fee 37 C.F.R. 1.16(a) \$690.00
Total Claims (37 CFR 1.16(c))	27	- 20 =	7	x \$ 18.00	\$126.00
Independent Claims (37 CFR 1.16(b))	4	- 3 =	1	x \$78.00	\$78.00
Multiple Dependent Claim(s), if any (37 CFR 1.16(d))			+	\$260.00	\$0

- ☐ Amendment canceling extra claims is enclosed.
☐ Amendment deleting multiple-dependencies is enclosed.
☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d).

Filing Fee Calculation \$ 894.00

- B. ☐ Design application
(\$330.00—37 CFR 1.16(f))
Filing Fee Calculation \$ _____
- C. ☐ Plant application
(\$540.00—37 CFR 1.16(g))
Filing Fee Calculation \$ _____

11. Small Entity Statement(s)

- ☐ Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is (are) attached.

WARNING:

"Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under § 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under § 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this section." 37 CFR 1.28(a)(2).

(complete the following, if applicable)

- ☐ Status as a small entity was claimed in prior application _____, filed on _____ from which benefit is being claimed for this application under:

35 U.S.C. § ☐ 119(e),
☐ 120,
☐ 121,
☐ 365(c),

and which status as a small entity is still proper and desired.

- ☐ A copy of the statement in the prior application is included.
Filing Fee Calculation (50% of A, B or C above) \$ _____

NOTE: Any excess of the full fee paid will be refunded if a small entity status is established refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under § 1.136. 37 CFR 1.28(a).

12. Request for International-Type Search (37 C.F.R. 1.104(d)) *(complete, if applicable)*

- ☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made at This Time

☒ Not Enclosed

☐ No filing fee is to be paid at this time.
(This and the surcharge required by 37 C.F.R. 1.16(e) can be paid subsequently.)

☐ Enclosed

☐ Filing fee \$ _____

☐ Recording assignment
(\$40.00; 37 C.F.R. 1.21(h))
(See attached "COVER SHEET FOR
ASSIGNMENT ACCOMPANYING NEW
APPLICATION.") \$ _____

☐ Petition fee for filing by other than
all the inventors or person on behalf
of the inventor where inventor
refused to sign or cannot be reached
(\$130.00; 37 C.F.R. 1.47 and 1.17(i)) \$ _____

☐ For processing an application with a
specification in a non-English language
(\$130.00; 37 C.F.R. 1.52(d) and 1.17(k)) \$ _____

☐ Processing and retention fee
(\$130.00; 37 C.F.R. 1.53(d) and 1.21(l)) \$ _____

☐ Fee for international-type search report
(\$40.00; 37 C.F.R. 1.21(e)) \$ _____

NOTE: 37 CFR 1.21(l) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 CFR 1.53(f) and this, as well as the changes to 37 CFR 1.53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1.21(l) must be paid, within 1 year from notification under § 53(f).

Total Fees Enclosed \$ _____

14. Method of Payment of Fees

☐ Check in the amount of \$ _____.

☐ Charge Account No. _____ in the amount of \$ _____.
A duplicate of this transmittal is attached.

15. Authorization to Charge Additional Fees

WARNING: If no fees are to be paid on filing, the following items should not be completed.

WARNING: Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. _____.

- ☐ 37 C.F.R. 1.16(a), (f) or (g) (filing fees)
☐ 37 C.F.R. 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: *Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.*

- ☐ 37 C.F.R. 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)
☐ 37 CFR 1.17(a)(1)-(5) (extension fees pursuant to § 1.136(a).
☐ 37 C.F.R. 1.17 (application processing fees)

NOTE: *"A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 CFR 1.136(a)(3).*

- ☐ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

NOTE: *Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b)).*

NOTE: *37 CFR 1.28(b) requires "Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . issue fee." From the wording of 37 CFR 1.28(b), (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.*

16. Instructions as to Overpayment

NOTE: *". . . Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 CFR 1.26(a).*

☐ Credit Account No. _____.

☐ Refund


SIGNATURE OF PRACTITIONER

Peter F. Corless

(type or print name of practitioner)

Reg. No. 33,860

Tel. No.: (617) 523-3400

Dike, Bronstein, Roberts & Cushman, LLP
130 Water Street

P.O. Address

Customer No.:

Boston, MA 02109

[X] Incorporation by reference of added pages

(check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

[X] Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added 5

[] Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added _____

[] Plus added pages deleting names of inventor(s) named on prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added _____

[] Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added _____

[] Statement Where No Further Pages Added

(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)

[] This transmittal ends with this page.

Express Mail Label No. EK4937941561
Docket No. 50439-2 CIP

U.S. PATENT APPLICATION

Title: ELECTROLYTIC COPPER PLATING SOLUTIONS

Inventors: Leon R. BARSTAD
James E. RYCHWALSKI
Mark LEFEBVRE
Stephane MENARD
James L. MARTIN
Robert A. SCHETTY, III
Michael TOBEN

Attorney: Peter F. Corless (Reg. No. 33,860)
Dike, Bronstein, Roberts & Cushman LLP
130 Water Street
Boston, MA 02109
Telephone: (617) 523-3400

ELECTROLYTIC COPPER PLATING SOLUTIONS

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to copper electroplating solutions, methods for using the solutions and products formed by using such methods and solutions. More particularly, the invention provides electrolytic copper plating solutions that have increased brightener levels and use of same for effective plating of high aspect ratio apertures, e.g. microvias with aspect ratios of at least 4:1 and diameters of 200 nm or smaller.

2. Background

Electroplating articles with copper coatings is generally well known in the industry. Electroplating methods involve passing a current between two electrodes in a plating solution where one electrode is the article to be plated. A common plating solution would be an acid copper plating solution containing (1) a dissolved copper salt (such as copper sulfate), (2) an acidic electrolyte (such as sulfuric acid) in an amount sufficient to impart conductivity to the bath and (3) additives (such as surfactants, brighteners, levelers and suppressants) to enhance the effectiveness and quality of plating. See generally U.S. Patents 5,068,013; 5,174,886; 5,051,154; 3,876,513; and 5,068,013 for a discussion of copper plating baths.

Over time, a number of improvements in electroplating techniques have been made as the articles to be plated evolved in degree of difficulty and standards for plating increased.

However, even with the improvements in electroplating techniques, circumstances exist that can lead to plating defects.

Copper plating technology has been particularly important in the manufacture of computer circuit boards. More specifically, during circuit board manufacture, copper electrical connections are provided between various board layers by plating board through holes whereby a thin conductive copper conductive is first applied, typically using electroless copper plating techniques, followed by electroplating copper from acid copper solutions.

Copper plating is also employed in circuit board manufacture to plate outer layers where final circuitry is defined. For such applications, panel plating is typically employed, where the full circuit board surface is copper plated followed by photodefining circuitry with a photoresist and then etching in a subtractive process. Alternatively an additive process can be employed, where copper circuits are produced by plating between lines defined by a resist relief image.

More recently, copper plating also has been employed in semiconductor chip manufacture to provide chip interconnections. Traditionally, semiconductors have been interconnected through aluminum conductors. However, industry continually demands enhanced performance, including ultra large-scale integration and faster circuits. Consequently, chip interconnects are required at dimensions of 200 nm and less. At such geometries, the resistivity of aluminum (theoretically 2.65×10^{-8} ohm/meter at room temperature) is considered too high to allow the electronic signal to pass at required speeds. Copper, with a theoretical resistivity of 1.678×10^{-8} ohm/meter, is considered a more suitable material to meet the next generation of semiconductor microchips.

Typical processes for defining semiconductor chip interconnects, particularly aluminum interconnects, have involved reactive ion etching of metal layers, e.g. a process that includes metal deposition, photolithographic patterning, line definition through reactive ion etching and dielectric deposition. However, in Cu-based systems, reactive ion etching is not practical as a result of the paucity of copper compounds with vapor pressures sufficient to enable removal of the copper as may be desired.

Consequently, alternative strategies have developed, such as the Damascene process. That process starts with deposition of dielectric typically by chemical vapor deposition of silicon materials or organic dielectrics followed by curing, or spin coating silicon materials or organic dielectrics. Patterning by photolithographic processes and reactive ion etching defines the vias and trenches (interconnects) in the dielectric. Barrier layers are then formed by chemical vapor deposition or other methods to isolate the copper lines from the dielectric. Copper is then deposited and excess material removed by chemical or mechanical polishing processes.

Although conventional copper plating systems can be suitable for plating vias and trenches as small as 300 nm with 4:1 aspect ratios, defects such as seams, voids and inclusions can occur with conventional methods when attempting to plate features that are smaller or have higher aspect ratios. Such defects can occur as a result of conformal copper plating, i.e. where all targeted surfaces are plated at the same rate such that the sidewalls of a via or trench plate together forming a seam or a demarcation of disruption where the copper grains are separated and will not anneal to form a continuous copper wire. Defects also will occur at the top rim of a via hole, where electronic charge density can concentrate and result in rapid copper growth that closes off the via before the via is filled sufficiently with metal. Such inadequate metal fill can result in inclusion and voids, disrupting the ability of the plated metal to carry a coherent signal.

A semiconductor wafer is generally plated with excess copper. However, as discussed above, problems can arise from the conventional copper plating. The typical defects that occur in the plating of the copper are for example, as discussed above, voids, inclusions and seams.

During the process of manufacturing an integrated circuit, a semiconductor wafer is often polished to remove the excess unwanted materials on the surface of the wafer. Polishing generally takes the form of chemical-mechanical planarization ("CMP") wherein a chemically active slurry is used in conjunction with a polishing pad. In a typical arrangement, the polishing pad is mounted on a rotatable platen, a slurry is fed onto the surface of the polishing pad, and the wafer is mounted in a carrier which urges the wafer against the surface of the moving polishing

pad with the slurry thereon. The unwanted material or excess copper is removed from the wafer.

It thus would be desirable to have new electroplating compositions. It would be particularly desirable to have new copper electroplating compositions that can plate effectively (e.g. absence of voids, inclusions and seams) high aspect ratio apertures, including high aspect ratio microvias and/or trenches as discussed above.

SUMMARY OF THE INVENTION

We have now found copper electroplating compositions that effectively plate a wide variety of articles, including printed circuit boards and other electronic packaging devices. Compositions and methods of the invention are particularly useful for filling microvias and trenches required by current and anticipated semiconductor fabrication requirements (including microvias having aspect ratios of at least 4:1 and diameters of 200 nm or less) by reliably plating copper deposits that are essentially or completely free of voids, inclusions or other plating imperfections.

Electroplating baths of the invention are characterized in significant part by comprising enhanced brightener concentrations. Without being bound by any theory, it is believed that the higher brightener concentrations can accelerate the plating rate in recesses and microvias as carrier molecules become incorporated into the plating deposit. This is counterintuitive to conventional thought and a completely unexpected result.

In particular, preferred electroplating compositions of the invention have a brightener concentration of at least about 1.5 mg per liter of plating solution (1.5 mg/L), more preferably a brightener concentration of at least about 1.75 mg per liter, still more preferably at least about 2.0, 2.5, 3, 3.5 or 4 mg of brightener per liter of plating solution. Good results have been achieved with even higher brightener concentrations, e.g. copper plating baths having a brightener concentration of at least about 5 mg per liter, or at least about 6, 7, 8, 9, 10, 12, 14, 16,

18, 20 or 25 mg/L, or even higher brightener concentrations such as at least about 30, 35, 40, 45, 50, 55 or 60 mg of brightener per liter of plating solution.

Preferably, the brightener concentration is maintained at such high concentrations
5 throughout the entire or at least substantial portion of a plating cycle. Such maintenance of brightener concentrations entails regular addition of brightener during a plating cycle as the brightener component plates out. Brightener concentrations and replenishment rates during a plating cycle can be readily determined by known methods, such as the CPVS method as disclosed in U.S. Patents 5,252,196 and 5,223,118, both assigned to the Shipley Company, or by
10 the cyclic voltammetric stripping (CVS) methods.

In addition to such an elevated brightener concentration, preferably the plating bath also contains a surfactant-type suppressor agent. It has been surprisingly found that use of such a suppressor agent in combination with elevated brightener concentrations can result in effective
15 "bottom-fill" copper plating of a microvia or other aperture without defects such as inclusions or voids. In particular, the suppressor enables enhanced plating rate at the bottom of a microvia, permitting copper to plate the entire aperture space in a substantially "bottom-fill" manner, without premature sealing of the aperture top that can result in inclusions or voids.

20 Another object of the invention is to improve the copper plating in the microvias of the semiconductor and avoid having voids, inclusions and seams in the microvias.

A further object of the invention is a process to remove excess material from a semiconductor wafer by using a chemical mechanical planarization process which comprises
25 contacting the semiconductor wafer with a rotating polishing pad thereby removing the excess material from the semiconductor wafer; wherein the semiconductor wafer has been prior electroplated by a copper electroplating composition comprising: at least one soluble copper salt, an electrolyte, and one or more brightener compounds that are present in a concentration of at least about 1.5 mg per liter of the electroplating composition.

The invention also includes articles of manufacture, including electronic packaging devices such as printed circuit boards, multichip modules, semiconductor integrated circuits and the like that contain a copper deposit produced from a plating solution of the invention. Other aspects of the invention are discussed *infra*.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a fragmental side elevation view partly broken away showing a wafer in a wafer carrier being polishing according to the invention.

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Figure 2 illustrates a bottom plan of an alternate groove polishing pad according to the invention.

Figures 3, A-F illustrate cross-sectional views of wall slopes of microvias and trenches having high aspect ratios.

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DETAILED DESCRIPTION OF THE INVENTION

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Compositions of the invention suitably contain a copper salt, an electrolyte preferably an acidic aqueous solution such as a sulfuric acid solution with a chloride or other halide ion source, and one or more brightener agents in enhanced concentrations as discussed above, and preferably a suppressor agent. The plating compositions also may contain other components such as one or more leveler agents and the like.

25

As discussed above, electroplating solutions of the invention are particularly effective in plating various articles having microvias with high aspect ratios and small diameters. In particular, solutions of the invention are useful in plating electronic packaging devices such as printed circuit boards, microchip module packaging and blind 3-dimensional structures, particularly semiconductor integrated circuits and other circuit systems. The electroplating solutions of the invention are particularly useful to copper fill microvias of such electronic devices without the defects exhibited upon use of prior chemistries. In addition, the invention has

application to plating on a wide variety of other polymer and metal substrates.

Electroplating solutions of the invention generally comprise at least one soluble copper salt, an electrolyte and a brightener component. More particularly, electroplating compositions of the invention preferably contain a copper salt; an electrolyte, preferably an acidic aqueous solution such as a sulfuric acid solution with a chloride or other halide ion source; and one or more brightener agents in enhanced concentrations as discussed above. Electroplating compositions of the invention also preferably contain a suppressor agent. The plating compositions also may contain other components such as one or more leveler agents and the like.

A variety of copper salts may be employed in the subject electroplating solutions, including for example copper sulfates, copper acetates, copper fluoroborate, and cupric nitrates. Copper sulfate pentahydrate is a particularly preferred copper salt. A copper salt may be suitably present in a relatively wide concentration range in the electroplating compositions of the invention. Preferably, a copper salt will be employed at a concentration of from about 10 to about 300 grams per liter of plating solution, more preferably at a concentration of from about 25 to about 200 grams per liter of plating solution, still more preferably at a concentration of from about 40 to about 175 grams per liter of plating solution.

Plating baths of the invention preferably employ an acidic electrolyte, which typically will be an acidic aqueous solution and that preferably contains a halide ion source, particularly a chloride ion source. Examples of suitable acids for the electrolyte include sulfuric acid, acetic acid, fluoroboric acid, methane sulfonic acid and sulfamic acid. Sulfuric acid is generally preferred. Chloride is a generally preferred halide ion. A wide range of halide ion concentrations (if a halide ion is employed) may be suitably utilized, e.g. from about 0 (where no halide ion employed) to 100 parts per million (ppm) of halide ion in the plating solution, more preferably from about 25 to about 75 ppm of halide ion source in the plating solution.

The invention also includes electroplating baths that are substantially or completely free of an added acid and may be neutral or essentially neutral (e.g. pH of at least less than about 8 or 8.5). Such plating compositions are suitably prepared in the same manner with the same components as other compositions disclosed herein but without an added acid. Thus, for
5 instance, a preferred substantially neutral plating composition of the invention may have the same components as the plating bath of Example 1 which follows, but without the addition of sulfuric acid.

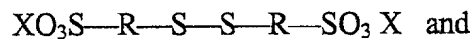
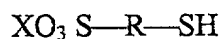
As discussed above, it has been discovered that by increasing brightener concentration
10 beyond conventional levels, uniform plating of particularly high aspect ratio microvias and other difficult-to-plate apertures is now possible.

In particular, copper electroplating compositions are provided that have a brightener agent concentration of at least about 1.5 mg per liter of plating solution (1.5 mg/L), compared to
15 typical brightener concentrations ranging from about 0.05 to 1.0 mg/L in prior composition. More preferably, in electroplating baths of the invention, the brightener concentration is at least about 1.75 mg/L, and still more preferably, at least about 2, 2.5, 3, 3.5 or 4 mg/L. Even higher brightener concentrations will be suitable or even preferred, e.g. at least about 10, 15, 20, 30, 40, 50 mg of brightener per liter of plating solution. A brightener concentration of from about 20 to
20 about 200 mg per liter of plating solution will be suitable for many applications.

Preferably, the brightener concentration is maintained throughout the entire electroplating process, or throughout at least a substantial portion of the plating process, e.g. at least about 50, 60, 70, 80 or 90 percent of the duration of the plating process. As discussed above, since
25 brightener levels are depleted as the electroplating progresses, the brightener component is preferably regularly replenished during plating to maintain a steady state brightener concentration.

A wide variety of brighteners, including known brightener agents, may be employed in the copper electroplating compositions of the invention. Typical brighteners contain one or more sulfur atoms, and typically without any nitrogen atoms and a molecular weight of about 1000 or less. Brightener compounds that have sulfide and/or sulfonic acid groups are generally preferred, particularly compounds that comprise a group of the formula $R'-S-R-SO_3X$, where R is an optionally substituted alkyl (which include cycloalkyl), optionally substituted heteroalkyl, optionally substituted aryl group, or optionally substituted heteroalicyclic; X is a counter ion such as sodium or potassium; and R' is hydrogen or a chemical bond (i.e. $-S-R-SO_3X$ or substituent of a larger compound). Typically alkyl groups will have from one to about 16 carbons, more typically one to about 8 or 12 carbons. Heteroalkyl groups will have one or more hetero (N, O or S) atoms in the chain, and preferably have from 1 to about 16 carbons, more typically 1 to about 8 or 12 carbons. Carbocyclic aryl groups are typical aryl groups, such as phenyl and naphthyl. Heteroaromatic groups also will be suitable aryl groups, and typically contain 1 to about 3 N, O or S atoms and 1-3 separate or fused rings and include e.g. coumarinyl, quinolinyl, pyridyl, pyrazinyl, pyrimidyl, furyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, oxidizolyl, triazole, imidazolyl, indolyl, benzofuranyl, benzothiazol, and the like. Heteroalicyclic groups typically will have 1 to 3 N, O or S atoms and from 1 to 3 separate or fused rings and include e.g. tetrahydrofuranyl, thienyl, tetrahydropyranyl, piperdiny, morpholino, pyrrolindinyl, and the like. Substituents of substituted alkyl, heteroalkyl, aryl or heteroalicyclic groups include e.g. C_{1-8} alkoxy; C_{1-8} alkyl, halogen, particularly F, Cl and Br; cyano, nitro, and the like.

More specifically, useful brighteners include those of the following formulae:



where in the above formulae R is an optionally substituted alkyl group, and preferably is an alkyl group having from 1 to 6 carbon atoms, more preferably is an alkyl group having from 1 to 4 carbon atoms; Ar is an optionally substituted aryl group such as optionally substituted phenyl or naphthyl; and X is a suitable counter ion such as sodium or potassium.

Some specific suitable brighteners include e.g. n,n-dimethyl-dithiocarbamic acid-(3-sulfopropyl)ester; 3-mercapto-propylsulfonic acid-(3-sulfopropyl)ester; 3-mercapto-propylsulfonic acid (sodium salt); carbonic acid-dithio-o-ethylester-s-ester with 3-mercapto-1-propane sulfonic acid (potassium salt); bissulfopropyl disulfide; 3-(benzthiazolyl-s-thio)propyl sulfonic acid (sodium salt); pyridinium propyl sulfobetaine; 1-sodium-3-mercapto-propane-1-sulfonate; sulfoalkyl sulfide compounds disclosed in U.S. Pat. No. 3,778,357; the peroxide oxidation product of a dialkyl amino-thiox-methyl-thioalkanesulfonic acid; and combinations of the above. Additional suitable brighteners are also described in U.S. Pat. Nos. 3,770,598, 4,374,709, 4,376,685, 4,555,315, and 4,673,469, all incorporated herein by reference. Particularly preferred brighteners for use in the plating compositions of the invention are n,n-dimethyl-dithiocarbamic acid-(3-sulfopropyl)ester and bis-sodium-sulfonopropyl-disulfide.

In addition to the copper salts, electrolyte and brightener, plating baths of the invention optionally may contain a variety of other components, including organic additives such as suppressors agents, leveling agents and the like.

As discussed above, use of a suppressor agent in combination with an enhanced brightener concentration is particularly preferred and provides surprisingly enhanced plating performance, particularly in bottom-fill plating of small diameter and/or high aspect ratio microvias.

Without being bound by any theory, it is believed such enhanced bottom-fill plating may occur due to the concentration of the suppressor agent being comparatively decreased at a bottom of a microvia as a result of diffusion effects through the length of the microvia. That reduced suppressor concentration results in an enhanced copper plating rate at the microvia bottom regions.

In contrast, at the surface of the article to be plated (at the top of the microvia), the suppressor agent concentration remains relatively constant and at an elevated level relative to the microvia bottom regions. Consequently, the area at a microvia top has a comparatively suppressed plating rate because of the enhanced suppressor agent concentration relative to the microvia bottom regions.

Preferred suppressor agents for use in the compositions of the invention are polymeric materials, preferably s having hetero atom substitution, particularly oxygen linkages. Generally preferred suppressor agents ate generally high molecular weight polyethers, such as those of the following formula:



where R is an aryl or alkyl group containing from about 2 to 20 carbon atoms; each X, Y, X' and Y' is independently hydrogen; alkyl preferably methyl, ethyl or propyl; aryl such as phenyl; aralkyl such as benzyl, and preferably one or more of X, Y, X' and Y' is hydrogen; and n is an integer between 5 and 100,000. Preferably, R is ethylene and n is greater than 12,000.

More specifically, surfactants useful in the present invention include e.g. amines such as ethoxylated amines, polyoxyalkylene amines and alkanol amines; amides; polyglycol-type wetting agents, such as polyethylene glycols, polyalkylene glycols and polyoxyalkylene glycols; high molecular weight polyethers; polyethylene oxides (mol. wt. 300,000 to 4 million); block copolymers of polyoxyalkyenes; alkylpolyether sulfonates; complexing surfactants such as alkoxyated diamines; and complexing agents for cupric or cuprous ions which include entprol, citric acid, edetic acid, tartaric acid, potassium sodium tartrate, acetonitrile, cupreine and pyridine.

Particularly suitable surfactants for plating compositions of the invention are commercially available polyethylene glycol copolymers, including polyethylene glycol copolymers. Such polymers are available from e.g. BASF (sold by BASF under Tetronic and Pluronic tradenames), and copolymers from Chemax. A butylalcohol-ethylene oxide-propylene

oxide copolymer having an M_w of about 1800 from Chemax is particularly preferred.

Surfactants are typically added to copper electroplating solutions in concentrations ranging from about 1 to 10,000 ppm based on the weight of the bath, more preferably about 5 to 10,000 ppm.

Use of one or more leveling agents in plating baths of the invention is generally preferred. Examples of suitable leveling agents are described and set forth in U.S. Pat. Nos. 3,770,598, 4,374,709, 4,376,685, 4,555,315 and 4,673,459. In general, useful leveling agents include those that contain a substituted amino group such as compounds having $R-N-R'$, where each R and R' is independently a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group. Typically the alkyl groups have from 1 to 6 carbon atoms, more typically from 1 to 4 carbon atoms. Suitable aryl groups include substituted or unsubstituted phenyl or naphthyl. The substituents of the substituted alkyl and aryl groups may be, for example, alkyl, halo and alkoxy.

More specifically, suitable leveling agents include e.g. 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine; 2-mercaptothiazoline; ethylene thiourea; thiourea; alkylated polyalkyleneimine; phenazonium compounds disclosed in U.S. Pat. No. 3,956,084; N-heteroaromatic rings containing polymers; quaternized, acrylic, polymeric amines; polyvinyl carbamates; pyrrolidone; and imidazole. A particularly preferred leveler is 1-(2-hydroxyethyl)-2-imidazolidinethione. Typical concentrations of leveling agents range from about 0.05 to 0.5 mg per liter of plating solution.

The copper electroplating compositions are suitably used in similar manner as prior copper electroplating baths, except an elevated brightener concentration is employed and preferably maintained at an elevated level throughout a plating cycle.

For instance, with reference to a printed circuit board substrate, a copper clad plastic substrate is typically employed, e.g. a copper clad glass fiber reinforced epoxy panel. Prior to formation of a circuit, apertures, such as microvias, are formed in the board by drilling and metallization. Microvias and other apertures also may be formed by photoimaging. Processes
5 for forming such apertures in electronic device substrates are known and are disclosed e.g. in U.S. Patent 4,902,610; C. Coombs, *Printed Circuits Handbook*, (4th ed., McGraw Hill); and T. Kiko, *Printed Circuit Board Basics* (PMS Indus.).

After formation of the microvia or other aperture, electroless plating procedures are then used to form a first metallic coating over the substrate surfaces and electrolytic copper deposition is then used to enhance the thickness of the coating. Alternatively, electrolytic copper may be plated directly over a suitably prepared microvia as disclosed in any of U.S. Pat. Nos. 5,425,873; 5,207,888; and 4,919,768. The next step in the process comprises electroplating copper onto the thus prepared conductive microvias using an electroplating solution of the invention.

Plating baths of the invention are preferably employed at or above room temperature, e.g. up to and somewhat above 65° C. The plating composition is preferably agitated during use such as by air sparger, work piece agitation, impingement or other suitable method. Plating is preferably conducted at a current ranging from 1 to 40 ASF depending upon substrate
20 characteristics. Plating time may range from about 5 minutes to 1 hour or more, depending on the difficulty of the work piece. See generally the examples which follow for exemplary preferred procedures.

A wide variety of substrates may be plated with the compositions of the invention, as
25 discussed above. The compositions of the invention are particularly useful to plate difficult work pieces, such as circuit board substrates with small diameter, high aspect ratio microvias and other apertures. The plating compositions of the invention also will be particularly useful for plating integrated circuit devices, such as formed semiconductor devices and the like. The compositions of the invention are particularly suitable for plating high aspect ratio microvias and trenches,

such as those having aspect ratios of 4:1 or greater. Figures 3 A-C show cross-sectional views of different wall slopes of trenches that may be plated according to the invention. Figures 3 D-F show cross-sectional views of different wall slopes of microvias that may be plated according to the invention. See the examples which follow for exemplary substrates plated in accordance with the invention.

As discussed above, aspect ratios of at least 4:1, having diameters of about 200 nm or smaller have been effectively copper plated with no defects (e.g. no voids or inclusions by ion beam examination) using plating solutions of the invention. Microvias with diameters below 150 nm, or even below about 100 nm, and aspect ratios of 5:1, 6:1, 7:1, 10:1 or greater, and even up to about 15:1 or greater can be effectively plated (e.g. no voids or inclusions by ion beam examination) using plating solutions of the invention.

Once the semiconductor wafer is plated, the wafer is preferably subjected to chemical-mechanical planarization (CMP). A CMP procedure can be conducted in accordance with the invention as follows. Figure 1 illustrates an apparatus 10 according to the invention. The apparatus 10 contains a polishing pad 12. The polishing pad 12 can be a conventional smooth polishing pad or a grooved polishing pad 12A, as shown in Figure 2. Examples of a grooved polishing pad 12A are described in United States Patent Nos. 5,177,908; 5,020,283; 5,297,364; 5,216,843; 5,329,734; 5,435,772; 5,394,655; 5,650,039; 5,489,233; 5,578,362; 5,900,164; 5,609,719; 5,628,862; 5,769,699; 5,690,540; 5,778,481; 5,645,469; 5,725,420; 5,842,910; 5,873,772; 5,921,855; 5,888,121; 5,984,769; and European Patent 806267. The polishing pad 12 can be located on a conventional platen 14 can rotate the polishing pad 12. The polishing pad 12 can be held on the platen 14 by a holding means 13, such as, but not limited to, an adhesive, such as, two faced tape having adhesive on both sides.

The semiconductor wafer 16 has one or more microvias and the copper has been electrolytically deposited onto the semiconductor wafer from an electroplating composition that comprises at least one soluble copper salt, an electrolyte, and one or more brightener compounds

that are present in a concentration of at least about 1.5 mg per liter of the electroplating composition. The wafer 16 is mounted in a wafer carrier 18 which urges the wafer 16 against the surface of the moving polishing pad 12. A polishing solution or slurry 20 is fed onto the polishing pad 12. The wafer carrier 18 can be at a different positions on the polishing pad 12.

5 The wafer 16 can be held in position by any suitable holding means 22 such as, but is not limited to, a wafer holder, vacuum or liquid tensioning such as, but not limited to a fluid such as, but not limited to water. If the holding means 22 is by vacuum then there is preferably a hollow shaft 24 which is connected to the wafer carrier 18. Additionally, the hollow shaft 24 could be used to regulate gas pressure, such as, but not limited to air or an inert gas or use a vacuum to initially hold the wafer 16. The gas or vacuum would flow from the hollow shaft 24 to the carrier 18. The gas can urge the wafer 16 against the polishing pad 12 for the desired contour. The vacuum can initially hold the wafer 16 into position in the wafer carrier 18. Once the wafer 16 is located on top of the polishing pad 12 the vacuum can be disengaged and the gas pressure can be engaged to thrust the wafer 16 against the polishing pad 12. The excess or unwanted copper is then removed.

The platen 14 and wafer carrier 18 can be independently rotatable. Therefore, it is possible to rotate the wafer 16 in the same direction as the polishing pad 12 at the same or different speed or rotate the wafer 16 in the opposite direction as the polishing pad 12.

All documents mentioned herein are fully incorporated herein by reference. The following non-limiting examples are illustrative of the invention.

Example 1:

25 A preferred copper electroplating bath of the invention was prepared by admixing the following components in water. In the composition the brightener was bis-sodium-sulfonopropyl-disulfide and the suppressor was a polyethylene glycol polymer sold under the tradename PEG 8000 by Union Carbide.

Component	Concentration
CuSO ₄ 5H ₂ O	60 g/l
H ₂ SO ₄	225 g/l
Cl	50 ppm
Suppressor	1 g/l
Brightener	2.1 mg/l

Through hole walls of a printed circuit board substrate and microvias were plated as follows with the above plating composition. An air-agitated plating tank outfitted with multiple cathode rails and one rectifier was charged with the above copper plating solution. During plating, the following deposition conditions were employed: current density of 14.5 mA/cm²; waveform was DC; temperature plating bath was 25° C. After termination of the plating procedure, a microvia of the board substrate was examined. It was found that copper completely filled the microvia walls to provide a smooth uniform copper plate with no voids.

Example 2:

A further preferred copper electroplating bath of the invention was prepared by admixing the following components in water. In the composition the brightener was bis-sodium-sulfonopropyl-disulfide and the suppressor was a propylene glycol copolymer sold under the tradename L62D by BASF.

Component	Concentration
CuSO ₄ 5H ₂ O	70 g/l
H ₂ SO ₄	175 g/l
Cl	50 ppm
Suppressor	0.875 g/l
Brightener	2.4 mg/l

200 nm with 7:1 aspect ratio microvias of a back end of the line semiconductor microchip wafer were plated using the above plating composition. The wafer was electrically attached to a cathode and the plating solution was pumped onto the surface of the wafer while rotating at upwards of 200 RPM. Electrical current of 14.5 mA/cm² was applied with DC wave form at 25° C. After termination of the plating procedure, the microvias were filled with no defects as

determined by focused ion beam examination.

Example 3 (comparative example)

A further preferred copper electroplating bath of the invention was prepared by admixing the following components in water. In the composition the brightener was bis-sodium-sulfonopropyl-disulfide and the suppressor was a propylene glycol copolymer sold under the tradename L62D by BASF.

Component	Concentration
CuSO ₄ 5H ₂ O	60 g/l
H ₂ SO ₄	225 g/l
Cl	50 ppm
Suppressor	1 g/l
Brightener	0.35 mg/l

200 nm with 4:1 aspect ratio microvias of a semiconductor microchip wafer were plated using the above comparative plating composition under conditions as described in Example 2. After termination of the plating procedure, the microvias were examined by scanning electron microscopy (SEM) and focused ion beam examination. Those examinations showed the copper deposits in the microvias contained defects of voids, seams and inclusions.

Example 4:

A Patterned wafer from Sematech Q cleave D reticle lithography targeting 0.18 trenches etched in 7500 angstroms of PETEOS over 1500 angstroms of nitride over 5500 angstroms of SiO₂ then filled with 250 angstroms of tantalum barrier over 1000 angstroms of sputtered copper seed plated with 10,000 angstroms of copper from the preferred electroplated compositions of the invention having a brightener concentration of at least about 1.5 mg per liter of plating solution was polished on a rotary platform as described in Figure 1. A RODEL IC1000 urethane polishing pad with grooves along with a RODEL slurry containing abrasive particles was used to remove the excess plated copper via the CMP method. The platen rotation speed was 430 RPM in a counter clockwise direction. The carrier rotation speed was 129 rpm in a counter clockwise

direction. The down force or pressure applied was 6 psi. Polish time was 50 sec. The wafer was cleared to the tantalum barrier layer and examined for voids by focused ion beam scanning electron microscopy. No voids were found in the cross section nor in the top down view of the SEM on trenches 200nm wide and 1 micron deep to 2 microns wide and 1 micron deep.

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A belt polishing pad, web polishing pad, or a fixed abrasive pad with abrasive free chemistry or abrasive containing slurry can also be used. Grooves or asperities or contours in the pad are necessary for liquid transport in all cases.

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The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims.

What is claimed:

1. A copper electroplating composition comprising:
at least one soluble copper salt,
an electrolyte, and
one or more brightener compounds that are present in a concentration of at least about 1.5 mg per liter of the electroplating composition.
2. The composition of claim 1 wherein the concentration of the brightener agent is at least about 2 mg per liter of the electroplating composition.
3. The composition of claim 1 wherein the concentration of the brightener agent is at least about 4 mg per liter of the electroplating composition.
4. The composition of claim 1 wherein the concentration of the brightener agent is at least about 10 mg per liter of the electroplating composition.
5. The composition of claim 1 wherein the concentration of the brightener agent is at least about 25 mg per liter of the electroplating solution.
6. The composition of claim 1 wherein the one or more brightener compounds contain one or more sulfur atoms.
7. The composition of claim 1 wherein the one or more brightener compounds comprise one or more sulfide or sulfonic acid groups.
8. The composition of claim 1 wherein the one or more brightener compounds comprise a group of the formula $R'-S-RSO_3$ where R is optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted aryl, optionally substituted heteroaromatic, or

optionally substituted heteroalicyclic; and R' is hydrogen or a chemical bond.

9. The composition of claim 1 wherein the composition further comprises a suppressor agent.

10. The composition of claim 9 wherein the suppressor agent is a polyether.

11. The composition of claim 1 wherein the composition further comprises a leveler agent.

12. The composition of claim 1 wherein the electroplating composition is acidic.

13. A method for plating an electronic device substrate containing one or more apertures, the method comprising:

electrolytically depositing onto the substrate copper from an electroplating composition that comprises at least one soluble copper salt, an electrolyte, and one or more brightener compounds that are present in a concentration of at least about 1.5 mg per liter of the electroplating composition.

14. The method of claim 13 wherein the brightener concentration is at least about 2 mg per liter of the electroplating solution.

15. The method of claim 13 wherein the brightener concentration is at least about 10 mg per liter of the electroplating solution.

16. The method of claim 13 wherein the substrate is a printed circuit board substrate or semiconductor with one or microvias.

17. The method of claim 16 wherein the one or more microvias have an aspect ratio of at least about 4:1 and diameters of at least about 200 nm.

18. The method of claim 17 wherein copper is deposited to fill the one or more microvias to provide a copper plate in the absence of voids or inclusions.

19. The method of claim 17 wherein the composition further comprises a suppressor agent.

20. The method of claim 13 wherein the substrate is a microchip module substrate.

21. An article of manufacture comprising an electronic device substrate containing one or more apertures each having walls, the aperture walls having thereon an electrolytic copper deposit obtained from an electroplating composition that comprises at least one soluble copper salt, an electrolyte, and one or more brightener compounds that are present in a concentration of at least about 1.5 mg per liter of the electroplating composition.

22. The article of claim 21 wherein the substrate is printed board substrate, a microchip module substrate, or a semiconductor chip substrate.

23. The article of claim 21 wherein the substrate comprises the one or more microvias that have an aspect ratio of at least about 4:1 and diameters of at least about 200 nm, and the walls of the one or more microvias have a copper deposit that is free of voids.

24. A process to remove excess material from a semiconductor wafer by using a chemical mechanical planarization process which comprises contacting the semiconductor wafer with a rotating polishing pad thereby removing the excess material from the semiconductor wafer; wherein the semiconductor wafer has been prior electroplated by a copper electroplating composition comprising:

at least one soluble copper salt,

an electrolyte, and

one or more brightener compounds that are present in a concentration of at least about 1.5 mg per liter of the electroplating composition.

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25. The process as claimed in claim 24, wherein said polishing pad is grooved.

26. The process as claimed in claim 24, wherein the semiconductor wafer is also subjected to a polishing slurry.

27. A process to remove excess material from a semiconductor wafer by using a chemical mechanical planarization process which comprises contacting the semiconductor wafer with a rotating polishing pad thereby removing the excess material from the semiconductor wafer; wherein the semiconductor wafer has been prior electroplated by the composition of claim 1.

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ABSTRACT

The present invention provides *inter alia* copper electroplating compositions, methods for use of the compositions and products formed by the compositions. Electroplating compositions of the invention contain an increased brightener concentration that can provide effective copper
5 plate on difficult-to-plate aperture walls, including high aspect ratio, small diameter microvias.

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Fig. 1.

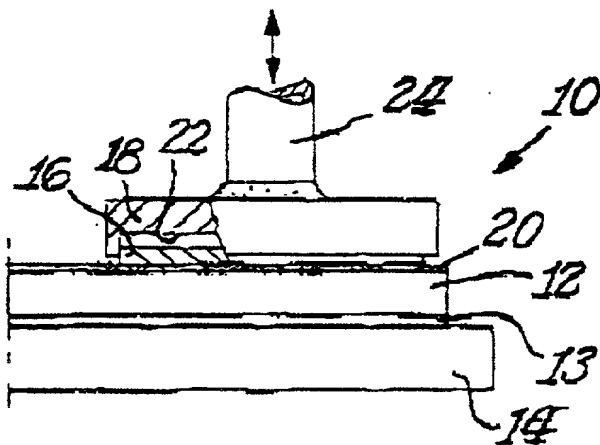


Fig. 2.

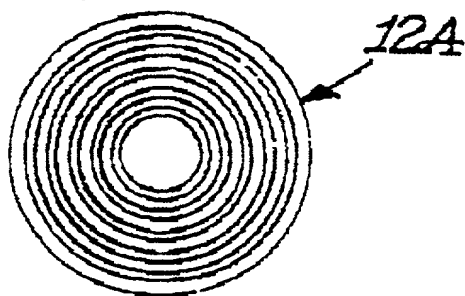
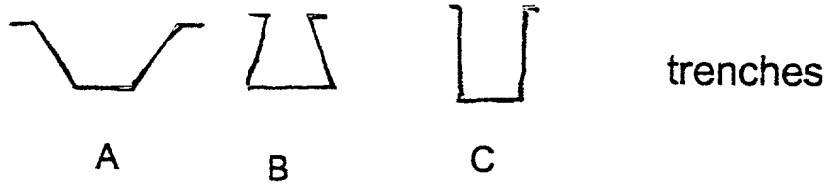


Fig. 3



**ADDED PAGES FOR APPLICATION TRANSMITTAL WHERE BENEFIT OF
PRIOR U.S. APPLICATION(S) CLAIMED**

NOTE: See 37 CFR 1.78.

17. Relate Back

WARNING: If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.

(complete the following, if applicable)

☒ Amend the specification by inserting, before the first line, the following sentence:

A. 35 U.S.C. 119(e)

NOTE: "Any nonprovisional application claiming the benefit of one or more prior filed copending provisional applications must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior provisional application, identifying it as a provisional application, and including the provisional application number (consisting of series code and serial number)." 37 C.F.R. § 1.78(a)(4).

☐ "This application claims the benefit of U.S. Provisional Application(s) No(s):

APPLICATION NO(S):

FILING DATE

_____	_____
_____	_____
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B. 35 U.S.C. 120, 121 and 365(c)

NOTE: "Except for a continued prosecution application filed under § 1.53(d), any nonprovisional application claiming the benefit of one or more prior filed copending nonprovisional applications or international applications designating the United States of America must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior application, identifying it by application number (consisting of the series code and serial number) or international application number and international filing date and indicating the relationship of the applications. . . . Cross-references to other related applications may be made when appropriate." (See § 1.14(a)). 37 C.F.R. § 1.78(a)(2).

☒ "This application is a

☐ continuation

☒ continuation-in-part

☐ divisional

of copending application(s)

☒ application number 09/313,045 filed on May 17, 1999.

☐ International Application _____ filed on _____ and which designated the U.S."

NOTE: The proper reference to a prior filed PCT application that entered the U.S. national phase is the U.S. serial number and the filing date of the PCT application that designated the U.S.

NOTE: (1) Where the application being transmitted adds subject matter to the International Application, then the filing can be as a continuation-in-part or (2) if it is desired to do so for other reasons then the filing can be as a continuation.

NOTE: The deadline for entering the national phase in the U.S. for an international application was clarified in the Notice of April 28, 1987 (1079 O.G. 32 to 46) as follows:

"The Patent and Trademark Office considers the International application to be pending until the 22nd month from the priority date if the United States has been designated and no Demand for International Preliminary Examination has been filed prior to the expiration of the 19th month from the priority date and until the 32nd month from the priority date if a Demand for International Preliminary Examination which elected the United States of America has been filed prior to the expiration of the 19th month from the priority date, provided that a copy of the international application has been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively. If a copy of the international application has not been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively, the international application becomes abandoned as to the United States 20 or 30 months from the priority date respectively. These periods have been placed in the rules as paragraph (h) of § 1.494 and paragraph (i) of § 1.495. A continuing application under 35 U.S.C. 365(c) and 120 may be filed anytime during the pendency of the international application."

☐ "The nonprovisional application designated above, namely application _____/_____, filed _____, claims the benefit of U.S. Provisional Application(s) No(s).:

APPLICATION NO(S).:

FILING DATE

_____/_____
_____/_____
_____/_____

☐ Where more than one reference is made above please combine all references into one sentence.

18. Relate Back—35 U.S.C. 119 Priority Claim for Prior Application

The prior U.S. application(s), including any prior International Application designating the U.S., identified above in item 17B, in turn itself claim(s) foreign priority(ies) as follows:

Country	Appln. no.	Filed
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The certified copy(ies) has (have)

☐ been filed on _____, in prior application _____, which was filed on _____.

☐ is (are) attached.

WARNING: *The certified copy of the priority application that may have been communicated to the PTO by the International Bureau may not be relied on without any need to file a certified copy of the priority application in the continuing application. This is so because the certified copy of the priority application communicated by the International Bureau is placed in a folder and is not assigned a U.S. serial number unless the national stage is entered. Such folders are disposed of if the national stage is not entered. Therefore, such certified copies may not be available if needed later in the prosecution of a continuing application. An alternative would be to physically remove the priority documents from the folders and transfer them to the continuing application. The resources required to request transfer, retrieve the folders, make suitable record notations, transfer the certified copies, enter and make a record of such copies in the Continuing Application are substantial. Accordingly, the priority documents in folders of international applications that have not entered the national stage may not be relied on. Notice of April 28, 1987 (1079 O.G. 32 to 46).*

19. Maintenance of Copendency of Prior Application

NOTE: *The PTO finds it useful if a copy of the petition filed in the prior application extending the term for response is filed with the papers constituting the filing of the continuation application. Notice of November 5, 1985 (1060 O.G. 27).*

A. ☐ Extension of time in prior application

(This item must be completed and the papers filed in the prior application, if the period set in the prior application has run.)

☐ A petition, fee and response extends the term in the pending **prior** application until _____.

☐ A **copy** of the petition filed in prior application is attached.

B. ☐ Conditional Petition for Extension of Time in Prior Application

(complete this item, if previous item not applicable)

☐ A conditional petition for extension of time is being filed in the pending **prior** application.

☐ A **copy** of the conditional petition filed in the prior application is attached.

20. Further Inventorship Statement Where Benefit of Prior Application(s) Claimed

(complete applicable item (a), (b) and/or (c) below)

- (a) ☐ This application discloses and claims only subject matter disclosed in the prior application whose particulars are set out above and the inventor(s) in this application are

☐ the same.

☐ less than those named in the prior application. It is requested that the following inventor(s) identified for the prior application be deleted:

(type name(s) of inventor(s) to be deleted)

- (b) ☐ This application discloses and claims additional disclosure by amendment and a new declaration or oath is being filed. With respect to the prior application, the inventor(s) in this application are

☐ the same.

☐ the following additional inventor(s) have been added:

(type name(s) of inventor(s) to be deleted)

- (c) ☐ The inventorship for all the claims in this application are

☐ the same.

☐ not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made

☐ is submitted.

☐ will be submitted.

21. Abandonment of Prior Application *(if applicable)*

- ☐ Please abandon the prior application at a time while the prior application is pending, or when the petition for extension of time or to revive in that application is granted, and when this application is granted a filing date, so as to make this application copending with said prior application.

NOTE: According to the Notice of May 13, 1983 (103, TMOG 6-7), the filing of a continuation or continuation-in-part application is a proper response with respect to a petition for extension of time or a petition to revive and should include the express abandonment of the prior application conditioned upon the granting of the petition and the granting of a filing date to the continuing application.

22. Petition for Suspension of Prosecution for the Time Necessary to File an Amendment

WARNING: "The claims of a new application may be finally rejected in the first Office action in those situations where (1) the new application is a continuing application of, or a substitute for, an earlier application, and (2) all the claims of the new application (a) are drawn to the same invention claimed in the earlier application, and (b) would have been properly finally rejected on the grounds of art of record in the next Office action if they had been entered in the earlier application." MPEP, § 706.07(b).

NOTE: Where it is possible that the claims on file will give rise to a first action final for this continuation application and for some reason an amendment cannot be filed promptly (e.g., experimental data is being gathered) it may be desirable to file a petition for suspension of prosecution for the time necessary.

(check the next item, if applicable)

☐ There is provided herewith a Petition To Suspend Prosecution for the Time Necessary to File An Amendment (New Application Filed Concurrently)

23. Small Entity (37 CFR § 1.28(a))

☐ Applicant has established small entity status by the filing of a statement in parent application No. _____.

☐ A copy of the statement previously filed is included.

WARNING: See 37 CFR § 1.28(a).

24. NOTIFICATION IN PARENT APPLICATION OF THIS FILING

☐ A notification of the filing of this
(check one of the following)

- ☐ continuation
- ☐ continuation-in-part
- ☐ divisional

is being filed in the parent application, from which this application claims priority under 35 U.S.C. § 120.